

THERMODYNAMICS

It is able to explain/predict

- direction
- equilibrium
- factors influencing the way to equilibrium

Follow the interactions during the chemical reactions

NO TIME SCALE !!!!

1

THE INTERNAL ENERGY

The energy of the system

$$E = E_{pot} + E_{kin} + U$$

$$E_{pot} = m \cdot g \cdot h$$

$$E_{kin} = \frac{1}{2} m \cdot v^2$$

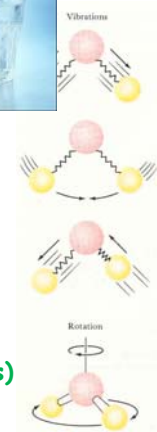
The internal energy

$$U = U_0 + U_{trans} + U_{rot} + U_{vibr} + U_{inter} + U_{exc}$$

chemical structure
(e.g. nucleus, chem. bonds)

thermal energy

intermolecular interactions



The absolute value of the internal energy U cannot be determined
only its change ΔU

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Interactions among particles

Strong 1	nuclear energy
Electromagnetic 10 ⁻²	among particles having charges or electric/magnetic momentum
	Coulomb 80-100 RT
	H-bridge 10-15 RT
	van der Waals 0.5-20 RT
	dispersion
	hydrophobic
Weak 10 ⁻¹⁴	nuclear reaction, thermonuclear fusions
Gravitational 10 ⁻³⁹	significant in cosmic ranges

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WE CANNOT STUDY THE WHOLE UNIVERSE AT THE SAME TIME



System: the part of the world which we have a special interest in. E.g. a reaction vessel, an engine, an electric cell.

Surroundings: everything outside the system.

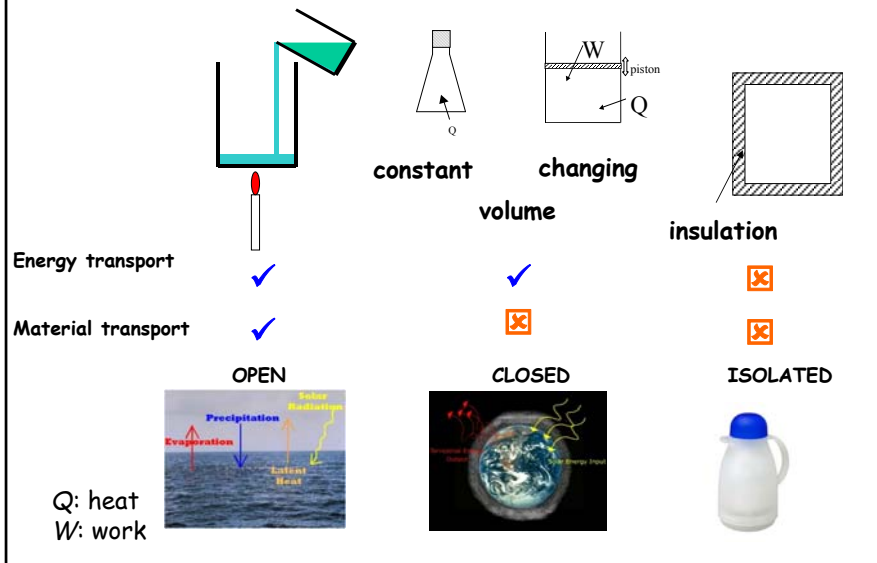
There are two points of view for the description of a system:

The system is a continuum,

(Particle view: the system is regarded as a set of particles, applied in *statistical methods* and *quantum mechanics*.)

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Classification based on the interactions between the system and its surrounding



Characterisation of the macroscopic state of the system

The state of a thermodynamic system is characterized by the collection of measurable physical properties.

- amount of substance: mass (m, g), chemical mass (n, mol)
- volume (V, m^3)
- pressure (p, Pa)
- temperature (T, K)
- concentration ($c, mol/L; x, -$)
- energy

State equation: relationship between the characteristics

e.g.: $pV = nRT$

$R = 8.314 \text{ J/molK}$

also diagrams, tables

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Classification of thermodynamic quantities:

Extensive quantities:

depend on the extent of the system and are additive:

mass (m)
volume (V)
internal energy (U), etc.

Intensive quantities:

do not depend on the extent of the system and are not additive :

temperature (T)
pressure (p)
concentration (c)

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CHANGES

A system is in thermodynamic **equilibrium** if none of the state functions are changing. In equilibrium no macroscopic processes take place. **Dynamic!!!!!!**

In a **non-equilibrium** system the state functions change in time, the system tends to be in equilibrium.

Meta-stable state: the state is not of minimal energy, energy is necessary for crossing an energy barrier.

A **reversible change** is one that can be reversed by an infinitesimal modification of one variable. A reversible process is performed through the same equilibrium positions from the initial state to the final state as from the final state to the initial state.

The following processes are frequently studied:

isothermal ($T = \text{const.}$)
isobaric ($p = \text{const.}$)
isochoric ($V = \text{const.}$)
adiabatic ($Q = 0$)

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State function: a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state (independent of path). A state function describes the equilibrium state of a system.

Important state functions in thermodynamics:

- U - internal energy
- H - enthalpy
- S - entropy
- A - Helmholtz free energy
- G - Gibbs free energy

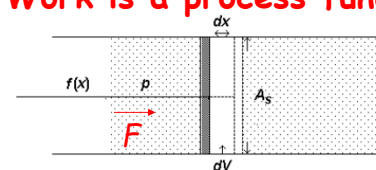
U, H, A, G change: Δ, d ; joule, J; kJ
 S J/K

Process functions: their values depend on the specific transition (or path) between two equilibrium states.

W, Q change: dW, dQ ; joule, J; kJ

Work is a process function

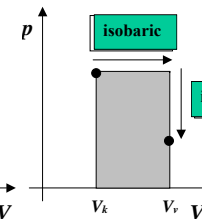
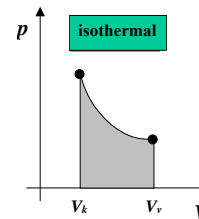
$$W_{mech} = \vec{F} \cdot \vec{\ell}$$



$$\delta W_{vol} = -pA_s dx = -pdV$$

sign convention

$$\delta W_{vol} = -pdV \quad W_{vol} = -\int_{V_i}^{V_f} pdV$$



isochoric

$$\int \frac{1}{x} dx = \ln|x| + c$$

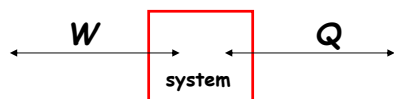
$$W_{vol} = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i}$$

isothermal work

$$W_{vol} = W_{vol,ibar} + W_{vol,ichor} = -p(V_f - V_i) + 0 = -p\Delta V$$

isobaric work

The FIRST LAW OF THERMODYNAMICS the conservation of energy



Isolated system:

$$dU = 0$$

Closed system

$$dU = dQ + dW$$

If no work:

$$dU = dQ$$

Convention: the system is in the focus

U state function, Q and W process function

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Processes at constant volume are well characterized by the internal energy. In chemistry (and in the environment) constant pressure is more frequent than constant volume. Therefore we define a state function which is suitable for describing processes at constant pressure:

$$H \equiv U + pV \quad \text{enthalpy}$$

THE CHARACTERISTICS OF THE ENTHALPY FUNCTION

Extensive quantity (depends on the amount of the material)

State function: similarly to the internal energy U only its change ΔH is known, not the absolute value

$$\Delta H = H_f - H_i = \int_f^i dH$$

It can be deduced that in isobaric conditions ($p=\text{const.}$)
if only pV work takes place:

$$dH = dQ$$

if other types of work:

$$dH = dQ + dW_1 + dW_2 + dW_3 + \dots$$

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1) HEAT

The heat is the transport of energy (without material transport) through the boundary of a system. The *driving force* is the gradient of the **temperature**.

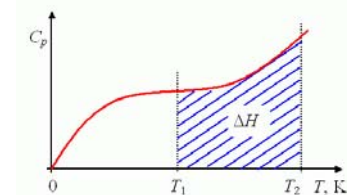
The heat (like the work) is not a state function.
We have to specify the path.

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A) Heating, cooling

$$Q = n \cdot \int_{T_1}^{T_2} C_m dT$$

C_m : **molar heat capacity**



Most frequently heating and cooling are performed either at constant pressure or at constant volume:

$$Q_p = n \int_{T_1}^{T_2} C_{mp} dT \quad Q_v = n \int_{T_1}^{T_2} C_{mv} dT$$

$C_{mp} > C_{mv}$ because heating at constant pressure is accompanied by pV work.

The difference is the most significant in case of gases

If $C_m \neq f(T)$ $Q = n \cdot C_m \cdot \Delta T$

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e.g., isobaric heating/cooling

$$\Delta H = Q_p = n \int C_{m,p}(T) dT$$

The molar heat capacity is generally expressed as a polynom:

$$C_{m,p} = a + bT + cT^{-2} + d \cdot T^2$$

After substituting into the integral expression

$$\Delta H = n \left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c(T_2^{-1} - T_1^{-1}) + \frac{d}{3}(T_2^3 - T_1^3) \right]$$

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B) Phase transition: isobaric+isothermic

Heat of... (latent heat)
evaporation - condensation
melting - freezing
sublimation - condensation

Molar heat of...

e.g.: molar enthalpy (=heat) of vaporisation; symbol: $\Delta H_m(\text{vap})$

C) Chemical reaction

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2. WORK: in general the work can be expressed as the product of an intensive quantity and the change of an extensive quantity:

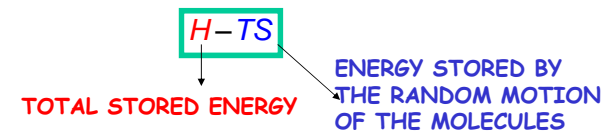
Type of work	Intensive quantity	Extensive quantity	Elementary work
pV	Pressure (-p)	Volume V	$dW = -pdV$
Surface	Surface tension (γ)	Surface (A)	$dW = \gamma dA$
Electric	Potential (φ)	Charge (q)	$dW = \varphi dq$

...

The work is an energy transport through the boundary of the system. The driving force (or potential function) is the gradient of the intensive parameter belonging to the process.

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CAN WE UTILIZE THE full ENTHALPY?



Entropy (S) measure of the disorder

$$Q_{rev} = T \cdot S$$

$$[S] = J/K$$

Each interaction can be characterized by an entropy change

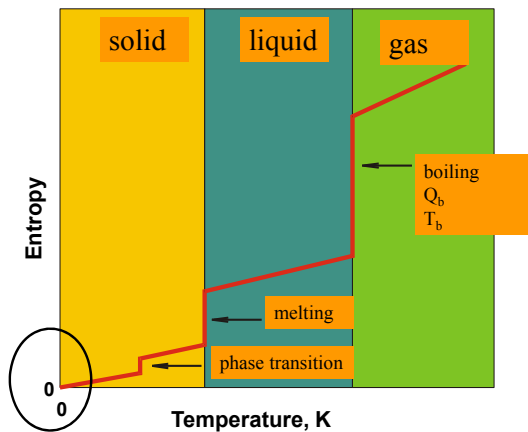
State function, extensive

$$S = nS_m$$

$$dQ_{rev} = T \cdot dS;$$

if only pV is performed: $\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$

CHANGE OF ENTROPY WITH TEMPERATURE



at $T=0$ K $S_{\text{thermal}}=0$ (no motion), but the atoms might be disordered: $S_{\text{configuration}} > 0$

The entropy of pure perfect crystals at 0 K is identical (3rd law). $S(0) \equiv 0$

The entropy unlike U and H has an absolute scale.

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If only pV work occurs:
$$\Delta S = \frac{Q_{\text{rev}}}{T} = \frac{\Delta H}{T}$$

Phase transitions: (isothermal-isobaric processes)

$$\Delta S(\text{melt}) = \frac{\Delta H(\text{melt})}{T_{\text{melt}}} \qquad \Delta S(\text{ev}) = \frac{\Delta H(\text{ev})}{T_b}$$

$S \uparrow$

- heating
- melting
- evaporation
- expansion

Disorder \uparrow

$S \downarrow$

- cooling
- freezing
- condensation
- compression

Disorder \downarrow

Heat input: more disordered motion

Work input: order

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Evaporation entropies at normal boiling point

	$\Delta S(\text{ev}), \text{JK}^{-1}\text{mol}^{-1}$
bromine	88.6
benzene	87.2
carbon tetrachloride	85.9
cyclohexane	85.1
hydrogen sulphide	87.9
ammonia	97.4
water	109.1
mercury	94.2

p -dependent
standard molar entropy
standard pressure (1 bar = 100000Pa=0.986 atm)²¹

Direction of natural processes

(spontaneity of processes)

- - $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$
- - gases fill the space available
- - hot objects cool to the temperature of their environment

Processes in nature: energy dissipation

Ordered \longrightarrow Disordered

? Which of the energetically „legal“ (conform with the 1st law of TD) will spontaneously take place?

Understanding the chemical processes and their equilibrium

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In isolated systems in spontaneous processes the change of entropy is positive: $\Delta S \geq 0$

It can be proved that if a spontaneous process occurs in an isolated system, S increases (2nd law).

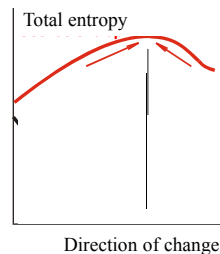
The equilibrium is reached when entropy has a maximum

If the system is not isolated:

$$\Delta S_{\text{system}} + \Delta S_{\text{environment}} \geq 0$$

The total entropy change of a process:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}}$$



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$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}}$$

if p, T constant:

$$\Delta S_{\text{environment}} = -\frac{\Delta H_{\text{system}}}{T} \quad \begin{matrix} \text{endothermic} \\ \text{exothermic} \end{matrix}$$

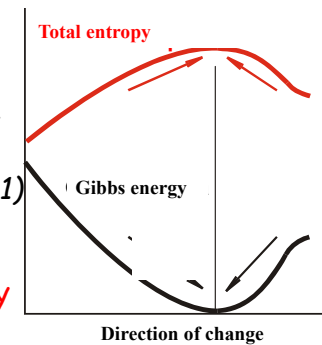
$$\Delta S_{\text{total}} = -\frac{\Delta H_{\text{system}}}{T} + \Delta S_{\text{system}} \quad / \cdot T$$

$$T\Delta S_{\text{total}} = -\Delta H_{\text{system}} + T\Delta S_{\text{system}} \quad / \cdot (-1)$$

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S \equiv \Delta G$$

$$G \equiv H - TS \quad \text{Gibbs FREE ENTALPY}$$

$$\Delta S = \frac{Q_{\text{rev}}}{T} = \frac{\Delta H}{T}$$



At constant temperature and pressure in a closed system if the process is spontaneous, G keeps decreasing, as long as the equilibrium is reached (the minimum of the G function) (unless no other work but pV).

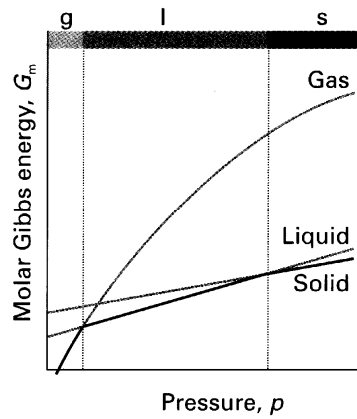
! Spontaneity \Leftrightarrow rate of reaction ! $G_{m,\text{graphite}} - G_{m,\text{diamond}} = -3 \text{ kJ} / \text{mol}$

$G \equiv H - TS$ FREE ENTALPY (GIBBS ENERGY)

$G(p)$ $T = \text{const.}$ State function

$G = H - TS$ $H \equiv U + pV$

$dG = Vdp$



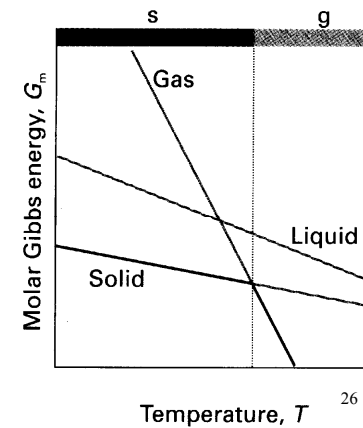
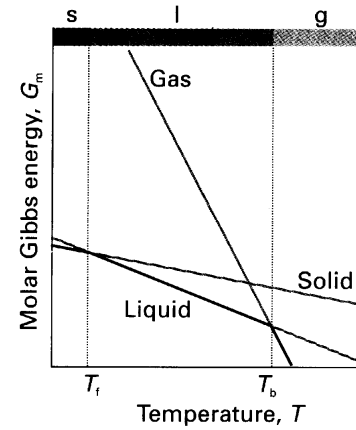
$\left(\frac{\partial G}{\partial p}\right)_T = V$

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$G(T)$ $p = \text{const.}$

$G = H - TS$ $H \equiv U + pV$

$dG = -SdT$ $\left(\frac{\partial G}{\partial T}\right)_p = -S$

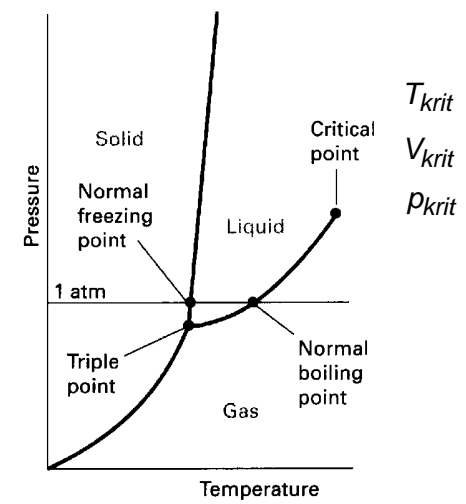


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PHASE EQUILIBRIUM IN PURE MATTER

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PHASE DIAGRAM



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EQUILIBRIUM OF PHASES

$$G_m(1) = G_m(2)$$

$$G_m(1) + dG_m(1) = G_m(2) + dG_m(2)$$

$$dG_m(1) = dG_m(2)$$

$$dG_m = V_m dp - S_m dT$$

$$dG_m(1) = V_m(1) dp - S_m(1) dT$$

$$dG_m(2) = V_m(2) dp - S_m(2) dT$$

$$V_m(1) dp - S_m(1) dT = V_m(2) dp - S_m(2) dT$$

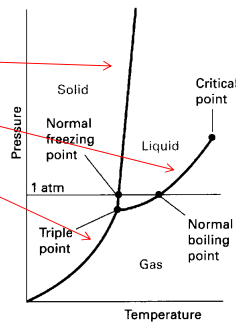
$$[S_m(2) - S_m(1)] dT = [V_m(2) - V_m(1)] dp$$

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

Phase transition is an isothermal and isobaric process:

$$\Delta S_m = \frac{\Delta H_m}{T} \quad \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$$

Clapeyron



PHASE DIAGRAM

Triple point

Critical point

T_{crit}

V_{crit}

P_{crit}

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GIBBS' PHASE RULE

$$F = C + P - 2$$

in non-reactive multi-component heterogeneous systems where the components and phases are in thermodynamic equilibrium with each other, the **degrees of freedom** The number of *degrees of freedom* F is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without determining one another.

Phase

a form of matter that is homogeneous in chemical composition and physical state

Typical phases are solids, liquids and gases.

≠ physical state !

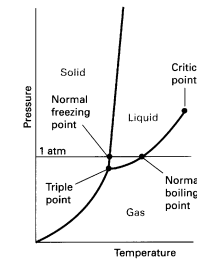
Phase boundary

Component, C

chemically independent constituents of the system

one-component system: a system involving one pure chemical

two-component system: mixtures of water and ethanol (two chemically independent components)



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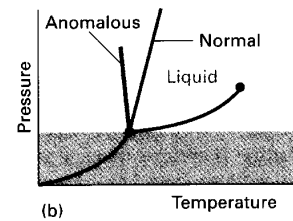
Standard

	heat of melting, kJ mol ⁻¹	heat of evaporation, kJ mol ⁻¹
acetone	5,72	29,1
ammonia	5,65	23,4
argon	1,2	6,5
benzene	9,87	30,8
ethanol	4,60	43,5
helium	0,02	0,08
mercury	2,29	59,30
methane	0,94	8,2
methanol	3,16	35,3
water	6,01	40,7

Standard pressure, at the temperature of the phase transition

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Answer of S/L interface on pressure



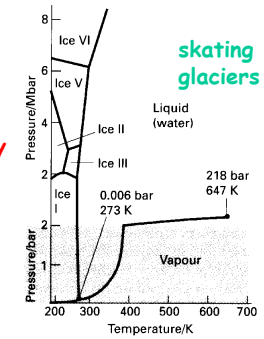
$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$(V_m dp)_{szil} \stackrel{?}{=} (V_m dp)_{foly}$$

Water

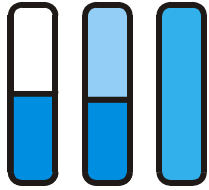
ice: 19,7 cm³/mol water: 0 cm³/mol

polimorphy



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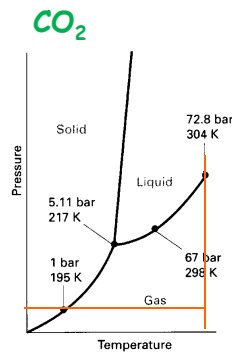
Critical state



Density
Diffusion
Solubility

$T_k < RT$ O_2, N_2, CO, CH_4

$T_k > RT$
 CO_2, NH_3, Cl_2, C_3H_8



Supercritical extraction
310-330 K
80-300 bar

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The liquid/gas transition: evaporation and condensation

standard (molar) evaporation
(at the boiling point, standard pressure)

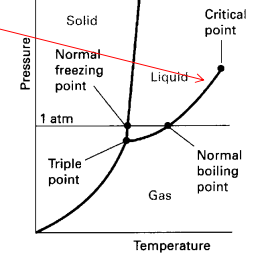
$$\frac{dp}{dT} = \frac{\Delta H_m(ev)}{T\Delta V_m}$$

Clapeyron

$$\Delta V = V_m(gáz) - V_m(foly) \cong V_m(gáz) \quad V_m(gas) = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{p\Delta H_m'(ev)}{RT^2}$$

Clausius-Clapeyron



The heat of evaporation of a pure liquid depends only on T

$$\int_{p_k}^{p_v} d \ln p = \int_{T_k}^{T_v} \frac{\Delta H'(ev)}{RT^2} dT$$

$$\frac{dp}{p} = d \ln p$$

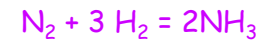
$$d(1/T)/dT = -1/T^2$$

$$\ln \frac{p_v}{p_k} = \frac{\Delta H_m'(ev)}{R} \left(\frac{1}{T_k} - \frac{1}{T_v} \right)$$

$$\frac{dT}{T^2} = -d \frac{1}{T} \quad 34$$

CHEMICAL EQUILIBRIUM

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Generally: v is the stoichiometric factor, M is the chemical formula, $_k$ is for reactants, $_t$ is for products:

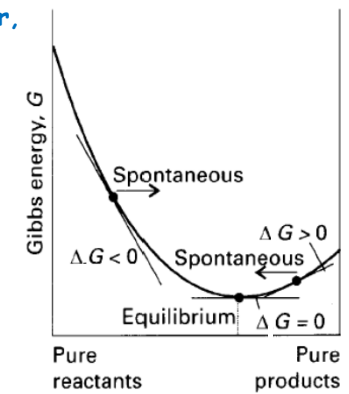
$$\sum v_k M_k = \sum v_t M_t$$

Each compound can be characterized with a Gibbs energy

Thus, similarly to the heat of reactions, the Gibbs energy of the chemical reaction is

$$\Delta_r G = \sum v_t G_t - \sum v_k G_k \quad p \text{ and } T \text{ const}$$

Spontaneous change: $\Delta_r G < 0$, p and T const.
In equilibrium: $\Delta_r G = 0$, p and T const.



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When is a reaction thermodynamically feasible ?

$$\Delta_r G = \Delta_r H - T \Delta_r S \leq 0$$

ΔH	ΔS	$\Delta G < 0$
-	+	at any temperature
+	-	no such temperature
-	-	if $T < \frac{\Delta H}{\Delta S}$
+	+	if $T > \frac{\Delta H}{\Delta S}$

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Relationship of standard Gibbs energy and equilibrium constant

$$\Delta_r G^\ominus = -RT \ln K$$

$\Delta_r G^\ominus$ the standard Gibbs energy of the chemical reaction

\ominus refers to the standard state (standard pressure: $p^\ominus = 10^5 \text{ Pa} = 1 \text{ bar}$); temperature is not fixed but most data are available at 298 K

$$K = \frac{\prod a_{t,e}^{v_t}}{\prod a_{k,e}^{v_k}} \approx \frac{\prod c_{t,e}^{v_t}}{\prod c_{k,e}^{v_k}}$$

Thermodynamic equilibrium constant (unitless)

$a = c\gamma$ a: (chemical) activity
 γ : activity coefficient

c_e : equilibrium composition

The equilibrium constant is a very important quantity in thermodynamics. It characterizes several types of equilibria of chemical reactions

~ in gas, liquid, and solid-liquid phases;

~ in different types of reactions between neutral and charged reactants

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The equilibrium constant can be expressed using several parameters like pressure, mole fraction, (chemical) concentration, molality.

Relationship between thermodynamic K and macroscopic parameters (how can we calculate K from measured data)

thermodynamic K

	$K = \frac{\prod a_B^{v_B}}{\prod a_A^{v_A}}$	
ideal gas	$K = K_p \cdot (p^0)^{-\Delta v}$	$K_p = \frac{\prod p_B^{v_B}}{\prod p_A^{v_A}}$
solutions	$K = K_\gamma \cdot K_c \cdot (c^0)^{-\Delta v}$	$K_\gamma = \frac{\prod \gamma_B^{v_B}}{\prod \gamma_A^{v_A}}$ és $K_c = \frac{\prod c_B^{v_B}}{\prod c_A^{v_A}}$

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When is a reaction thermodynamically feasible ?

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

$$\Delta_r G^\ominus = -RT \ln K$$

K ? 1

ΔH	ΔS	$\Delta G < 0$
-	+	at any temperature
+	-	no such temperature
-	-	if $T < \frac{\Delta H}{\Delta S}$
+	+	if $T > \frac{\Delta H}{\Delta S}$

Efficient product formation: $K \gg 1$, $K > 10^3$

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How can we influence K ?

1. Pressure? $\Delta_r G^\ominus = -RT \ln K$ As G^\ominus is defined at standard pressure, no p influence

2. Temperature?

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$

$$\ln K' = -\frac{\Delta_r G^{\ominus'}}{RT'} = -\frac{\Delta_r H^\ominus}{RT'} + \frac{\Delta_r S^\ominus}{R}$$

$$\ln \frac{K'}{K} = \frac{\Delta_r H^\ominus}{RT} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

It is the standard reaction enthalpy
(~ heat of the reaction)
that determines
the temperature dependence of K

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$$\ln \frac{K'}{K} = \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

endothermic reactions (heat is absorbed from the environment, i.e., $\Delta_r H^\ominus > 0$) the right hand side is positive, so $\ln K - \ln K' > 0$ with increasing temperature.

exothermic reactions (heat is released to the environment, i.e., $\Delta_r H^\ominus < 0$) so $\ln K - \ln K' < 0$ with increasing temperature

Le Chatelier-Brown Principle: The equilibrium shifts towards the endothermic direction if the temperature is raised, and into the exothermic direction if the temperature is lowered. For exothermic reactions low temperature favours the equilibrium but at too low temperatures the rate of reaction becomes very low. An optimum temperature has to be found.

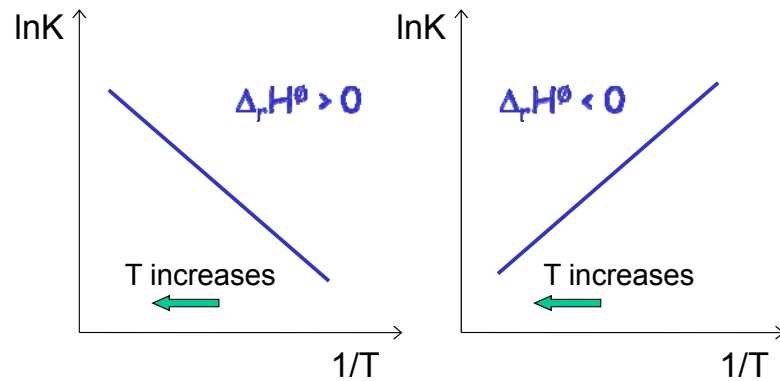
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$$\ln \frac{K'}{K} = \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

lnK - 1/T diagram for

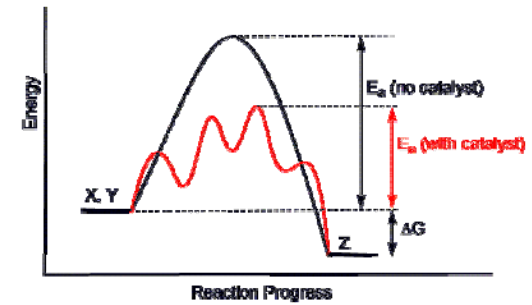
endothermic reaction

exothermic reaction



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3. Catalysis



Only the activation energy is influenced.
As ΔG is a state function, this has no influence either on its value, or on K.

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Influence of external conditions on equilibrium composition

$$K = \frac{\Pi a_{t,e}^{v_t}}{\Pi a_{k,e}^{v_k}} \approx \frac{\Pi c_{t,e}^{v_t}}{\Pi c_{k,e}^{v_k}}$$

Taking advantage to Le Chatelier-Brown Principle:

If the equilibrium concentration is modified, the system intends to reestablish the equilibrium

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Manipulation with pressure

Reactions where the volume decreases at constant pressure ($\Delta v < 0$) are to be performed at high pressure.

E.g. $\text{N}_2 + 3 \text{H}_2 = 2\text{NH}_3$ $\Delta v = -2$
Several hundred bars are used.

Reactions where the volume increases at constant pressure ($\Delta v > 0$) are to be performed at low pressure or in presence of an inert gas.

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EXERCISE 1

Problem:

The entropy of evaporation of cyclohexane at its normal boiling point (1 atm, 197.3 °C) is 85.1 J/(molK). Calculate its heat of evaporation at this temperature.

Solution:

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EXERCISE 2

Problem:

The boiling point of nitrogen is -196 °C. Estimate the change of entropy if 15 liter of liquid nitrogen is evaporated at atmospheric pressure ? The density of the liquid nitrogen is 0.81 g/cm³ ? What will be the sign of the change and explain why.

Solution:

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EXERCISE 3

Problem:

How much heat should be removed from the system if we intend to cool 5 m³ ethane gas from 140 °C to 30 °C ?

The temperature dependence of the molar heat can be neglected.

Solution: